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Effects of Reaction Temperature on the Formation of Polyurethane Prepolymer Structures

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ABSTRACT: For the first time, the molecular weight distribution and extent of side reactions have been quantified in polyurethane prepolymers. A combination of NMR, size exclusion chromatography, and mass spectrometry has been used to measure the molecular weight distribution. The values obtained are consistent with Flory's step polymerization theory. The type and amount of side reactions as a function of reaction temperature have also been investigated. At low temperature of reaction, the amount of branches arising from allophanate linkages is negligible. With only a relatively modest change in reaction temperature, this type of side reaction increases dramatically, so that at 145 °C as much as 10% of the nitrogens participate in allophanate linkages. The effect of this reaction on the molecular weight distribution was also measured. Upon formation of these side products, the molecular weight distribution broadens and the average increases. In this prepolymer system, the reactivity is independent of molecular weight.

Introduction

Polyurethane reactive hot melt adhesive is a relatively new system of study. In addition to environmental benefits, it combines many properties not found in other adhesives such as good bond durability, adhesion to a wide variety of substrates, high performance over a large temperature range, good chemical resistance, and fast set speed.[1,2] In all reactive polyurethane hot melt adhesives, the isocyanate functionalized prepolymers are a most crucial component. They provide the functional groups necessary for curing with moisture in the environment. They are also important in determining processing parameters necessary for property control. Despite the current commercial success and future potential, a number of structural aspects are ill-defined. This current study is concerned with two aspects of the prepolymer structure: the molecular weight distribution and a quantitative analysis of the possible side reactions.

The prepolymer is prepared by the reaction of a macrodiol such as poly(propylene glycol) or poly(caprolactone) with an excess of a diisocyanate. Because this reaction is a step polymerization, the prepolymer chains will have a molecular weight distribution. Several studies have examined the relationship between average molecular weight and properties such as curing dynamics and mechanical properties,[3−5] the largest factor being that the viscosity rises with an increase in molecular weight. What has been largely ignored is that the molecular weight distribution, not just the average value, must also affect the properties of the final cured material.

The curing reaction is shown in Scheme 1. An isocyanate group reacts with water, giving an unstable carbamic acid, which loses CO_2 to give an amine. This amine can than react with another isocyanate to give a urea linkage. Two main reactions are shown. In case 1, if both isocyanates arise from end-capped prepolymers, the resulting reaction will simply increase the molecular weight of the chains. In case 2, if free (monomeric) diisocyanate is consumed, the resulting reaction will incorporate hard segments into the chain. These hard segments provide physical cross-links in the adhesive, the volume fraction, and average length of which contribute to a polyurethane's modulus. The length of these hard segments is directly related to the amount of free diisocyanate. The prepolymer chain length will ultimately influence the molecular weight between cross-links and thus the elasticity of the final product. Thus, knowledge of the molecular weight distribution, and which variables perturb it, is critical to controlling the properties of these adhesives.

Several studies have used size exclusion chromatography (SEC) to follow the change in molecular weight distribution with time in order to observe reaction kinetics.[6−9] SEC has also been used to confirm the molecular weight distribution in model chain extension reactions between butanediol and diisocyanate.[10,11] Surprisingly, we know of no studies that have confirmed whether polyurethane prepolymers exhibit the most probable distribution when prepared in the bulk.

Side reactions are ubiquitous in urethane chemistry.[12−17] The possible reactions are shown in Scheme 2. Depending on whether a catalyst is present, these reactions can be favored over urethane formation. Our principal goal is to determine whether these side

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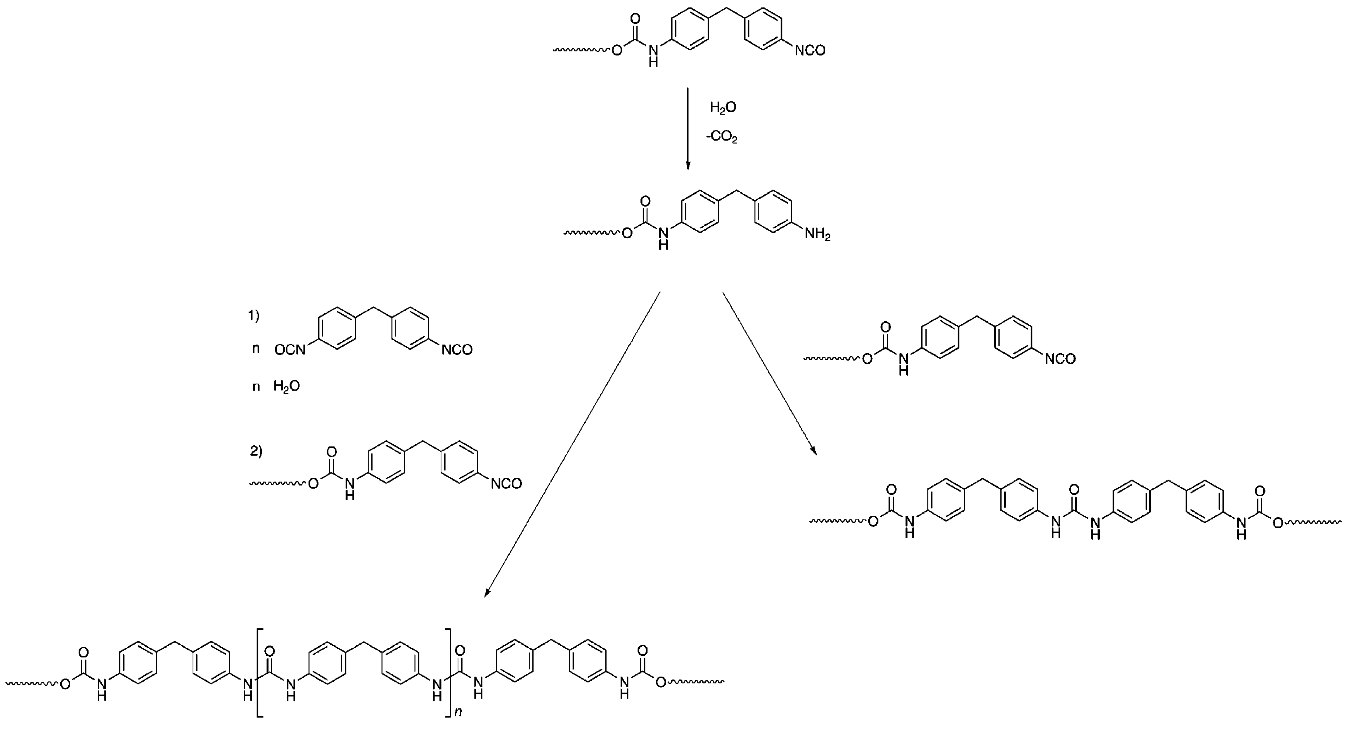
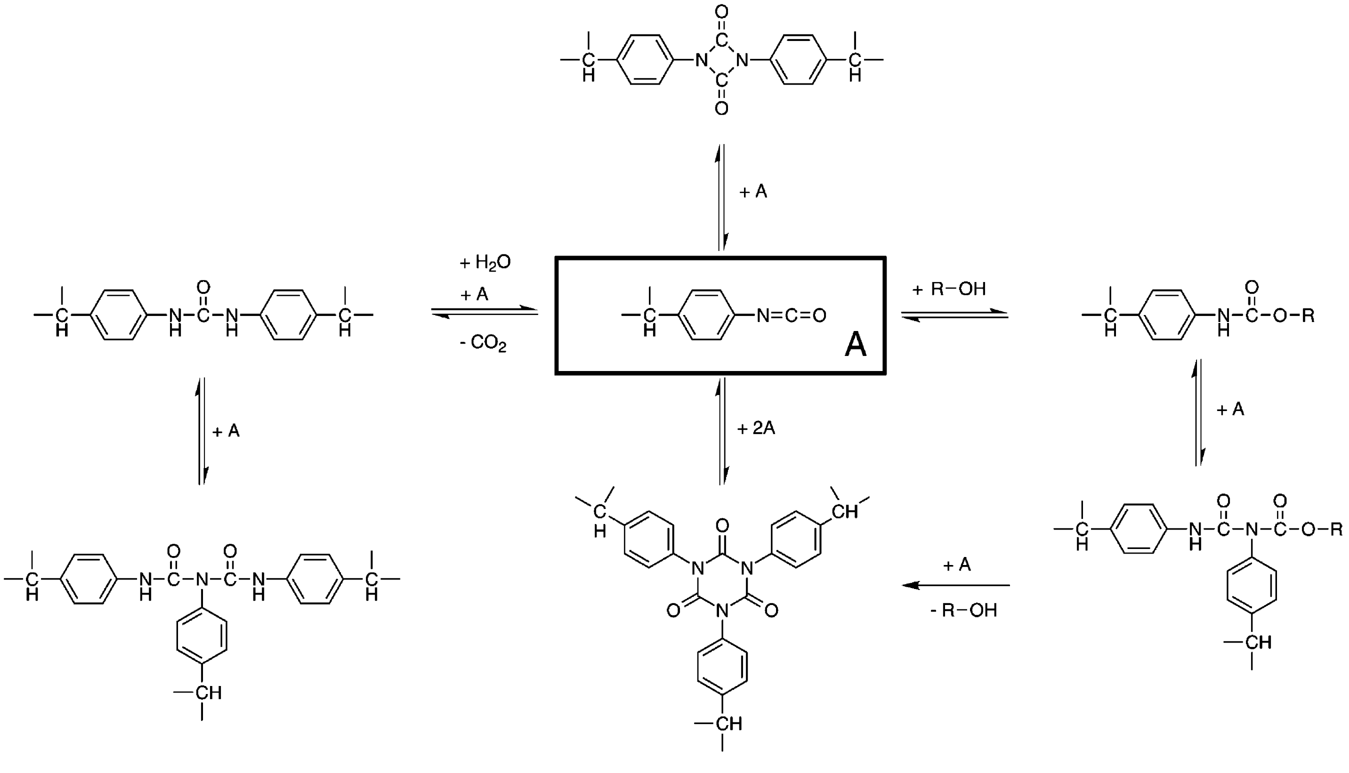
Scheme 1



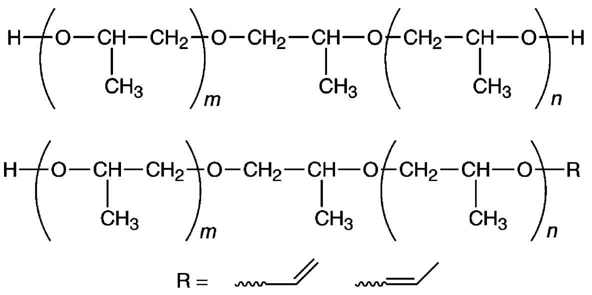
Scheme 2



products exist to any appreciable amount in a prepolymer system. Relatively few quantitative studies have been carried out to analyze the side product distribution of a prepolymer. The incorporation of the side reaction linkages, for example allophanate and isocyanurate, adds branch points, which both increases the viscosity of the prepolymer and changes the onset of gelation during cure.[18] These linkages also have different thermal stabilities than the urethane linkage.[19,20] If these reactions are significant, both pot stability, i.e., viscosity rise, and shelf life are expected to be dramatically affected. Evidence for these side reactions will also be a perturbed molecular weight distribution from the most probable one. Most notably, these reactions are expected to decrease the amount of free diisocyanate predicted.

In this paper, we have quantitatively characterized the molecular weight distribution and side product formation in a prepolymer prepared from poly(propylene glycol) (PPG) and methylene bis(phenyl isocyanate) (MDI). The reaction was carried out in the melt, at temperatures between 105 and 145 °C, with reaction

Scheme 3



times between 1 and 3 h, and in the absence of catalysts. Our goal is to understand whether these changes in processing conditions change the prepolymer structure. In addition, the relationship between side product formation and changes that occur in the molecular weight distribution will be determined. A combination of ^{1}H NMR, SEC, and mass spectrometry will be used, and our analysis is reported here.

Experimental Section

Materials. Poly(propylene glycol) (PPG) (Bayer 2056; 2000 g mol^{-1} with a hydroxyl value of 56) was dried in vacuo at 40 °C for at least 2 days prior to use. Trace impurities in the PPG can have a dramatic impact on the reaction kinetics and the side products formed. PPG is typically prepared by anionic polymerization, and depending on the initiator structure or end-capping procedure, the polymer may be terminated with primary hydroxyl groups, secondary hydroxyl groups, or both. Since the reactivity of these species is quite different (primary hydroxyls are approximately 3 times more reactive with isocyanates than secondary alcohols are), the identification of these end groups is important. We have determined that Bayer PPG 2056 is terminated with secondary hydroxyl groups by distortionless enhancement by polarization transfer (DEPT)[21] (in $CDCl_3$). Resonances observed at 66.63 ppm (dd, $J = 2.8$ and 121.5 Hz) correspond to the methynes adjacent to the hydroxyl group. This was also confirmed using ^{1}H NMR spectroscopy (in pyridine-d_5) where a doublet of sextuplets was observed at 4.18 ppm ($J = 4.2$ and 6.2 Hz), corresponding to the methyne adjacent to the hydroxyl group.[22]

In addition, chain transfer to monomer can occur in these systems, resulting in a small amount of allyl end groups and decreasing the ideal functionality from 2.0. Finally, trace amounts of base are known to greatly accelerate both urethane formation and side product formation.[16] Allyl end groups were evident in the ^{1}H NMR spectrum (in acetone-d_6) from a doublet of doublets at 5.19 ppm ($J = 10.5$ and 89.5 Hz). In addition, there is a multiplet at 5.90 ppm. This most likely arises from a 2-propenoxy end group, a constitutional isomer of the allyl end group. By integrating the resonances corresponding to hydroxyl ends and the two different alkene ends, the amount of allyl and 2-propenoxy end groups is found to be 2.62 and 2.28%, respectively. These groups are not expected to affect the outcome of prepolymer formation, though they will remain unreacted even after cure and will not contribute any cross-links.

Matrix-assisted laser desorption ionization time-of-flight (MALDI−TOF) mass spectroscopy was also used to characterize the starting PPG. On the basis of the mass of the peaks $\{76 + 58(m + n) + 23(\mathrm{Na}+)]\}$, the structure of the main component was determined as shown in Scheme 3. This component has $M_n = 2000$ with a PDI = 1.02. In addition, monofunctional chains with alkene end groups can be observed (allyl and 2-propenoxy have the same mass) since they have a different mass distribution $\{116 + 58(m + n) + 23(\mathrm{Na}+)\}$. The amount found by MALDI agreed well with the value found from ^{1}H NMR in the range from 2.5 to 5%.

Methylene diphenyl diisocyanate (MDI) (Aldrich, 98%) was used as received. In this case, its purity was checked prior to use by titration with butylamine.[23] The NCO content was found to be 7.84 mmol NCO g^{-1} MDI (98% pure). The impurity found is a dimer of MDI (uretidinedione), verified by its infrared-active C=O stretch at 1776 cm^{-1}. Urea was not present in the starting material.

Prepolymer Synthesis. The model prepolymers were prepared as follows. A three-neck round-bottom flask equipped with a stir bar, a nitrogen/vacuum adapter, and a rubber septum was charged with 20.0 g (19.99 mmol OH) of PPG. The system was evacuated to 100 mTorr and degassed by successive cycles of nitrogen fill/vacuum evacuation for at least 2 h at 100 °C. The water content at this point was found to be below the Karl Fisher limit (<0.02 wt %).[24] In the final step, the system was evacuated to 100 mTorr, closed, and equilibrated at the reaction temperature (108, 122, or 145 °C). 4.18 g of MDI (32.74 mmol of NCO) was melted in a second round-bottom flask, degassed, and added via syringe to the PPG. The reaction vessel was stirred under N_2 for 0.2−3 h to obtain the prepolymer. A small amount of the prepolymer was either titrated with dibutylamine (to measure the isocyanate content) or stirred with dry methanol for 24 h (to cap any unreacted isocyanate groups at ends).[25] The end-capped prepolymer is recovered via rotary evaporation.

Characterization. ^{1}H NMR spectra were recorded using a Bruker DPX300 spectrometer. The sample concentration was approximately 20 mg mL^{-1} in acetone-d_6. A recycle time (D_1) of 2.0 s was found to be long enough to allow relaxation of all protons. 512 scans were signal averaged. The hydroxyl-containing end groups could not be resolved from the backbone when acetone-d_6 was the solvent. To calculate the conversion, the samples were dissolved in pyridine-d_5. Resonances from the methyne adjacent to an alcohol and the methyne adjacent to a carbamate could be resolved clearly.[22] D_1 up to 30 s was not enough time to allow aromatic protons to relax. However, the methylene resonances showed no changes when D_1 was varied between 2 and 30 s.

MALDI−TOF mass spectra were recorded using a Reflex III MALDI−TOF (Bruker Daltonics) operating in linear mode using 24 kV acceleration voltage and 337 nm laser excitation. Solutions of 10 mg mL^{-1} PPG in $CHCl_3$ and 30 mg mL^{-1} dithranol in $CHCl_3$ were prepared and mixed together by volume in the ratio of 1:10. 1 μL of this solution was spotted onto a stainless steel target where sodium trifluoroacetate had been predeposited from MeOH (10 mg mL^{-1}of NaTFA in MeOH). A typical spectrum contains approximately 100 shots.

SEC was carried out with a Waters 510 HPLC pump equipped with three columns from Polymer Labs, Inc., having 5 μm bead size (two with MIXED-D and one 50 Å pore sizes). THF was used as the eluent. A Waters R401 differential refractometer was used as the detector. A SEC calibration curve of log(M_w) vs elution volume could be constructed for PPG prepolymers by combining the peak molecular weight (M_p) obtained from MALDI with curve fitting of the SEC traces. The SEC traces were fit as a series of Lorentzian functions. The first six of these with highest elution volumes are related to distributions that can be observed by MALDI−TOF. M_p was thus determined experimentally from MALDI−TOF. The last three Lorentzian functions were assigned M_p on the basis of the structure expected for those distributions. A third-order polynomial was used to fit the data in the range 1800−15 000 g mol^{-1}. The results are shown in Figure 1. The weight fraction distribution was determined on the basis of this calibration curve.

Results and Discussion

In this study, we aim to quantitatively characterize two aspects of the polyurethane prepolymer structure: the molecular weight distribution and the amount of side products. The combination involving NMR, SEC, and MALDI has proven to be extremely powerful in

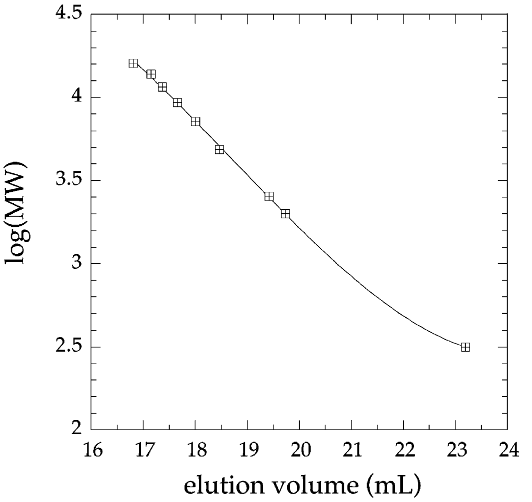


Figure 1. SEC calibration curve for MeOH end-capped PPG prepolymers.

Table 1. Reaction Conversion for Prepolymer Formation at 108 °C Calculated Using Various Methods

time (h)	ρ_{NCO} (titration)	ρ_{OH} (titration)	ρ_{OH} (NMR in pyr)	ρ_{NCO} (NMR in acet)
0.2	0.1037	0.1672	0.14	0.09
1.0	0.3984	0.6471	0.60	0.40
3.0	0.6000	0.9677	0.95	0.64

following the structural evolution during reaction. The specific features of each technique can be established by following the reaction to different degree of conversion at a specific temperature. Characterization of the structure obtained at different temperatures is then possible.

In this system, PPG is reacted with a stoichiometric excess of MDI (OH/NCO = r = 0.62) under an inert atmosphere in the absence of water. Prepolymer synthesis is an A−A + B−B step polymerization. At complete conversion, all of the hydroxyl groups will be consumed to form urethane groups and the degree of conversion, ρ_{OH}, is 1.0. Each urethane forming reaction also consumes an isocyanate, but since the isocyanates are in excess, at complete conversion $\rho_{NCO} = r\rho_{OH}$, or 0.62 in this case. In actual systems, ρ_{NCO} can be higher than predicted due to the many side reactions that can occur. The conversion (ρ_{NCO}) of the prepolymers prepared for reaction times of 0.2, 1, and 3 h at 108 °C is determined by reaction of the remaining isocyanate groups with a known excess of dibutylamine. The amount of remaining dibutylamine is then determined by titration with HCl. Assuming no side reactions, ρ_{OH} can be calculated, and the results are tabulated in Table 1. As expected, increasing the reaction time increases the conversion. After 3 h, urethane formation is nearly complete at 97% conversion.

^{1}H NMR spectroscopy can be used to directly determine ρ_{OH} of the prepolymers after first reacting the residual NCO with methanol. The degree of conversion obtained from ^{1}H NMR is consistently slightly lower than that determined from titration as shown in Table 1. The error in the conversion calculated from ^{1}H NMR is expected to be ~5%. The relative error associated with titration to be <0.2%. Taking into the experimental errors, the two methods yielded similar results.

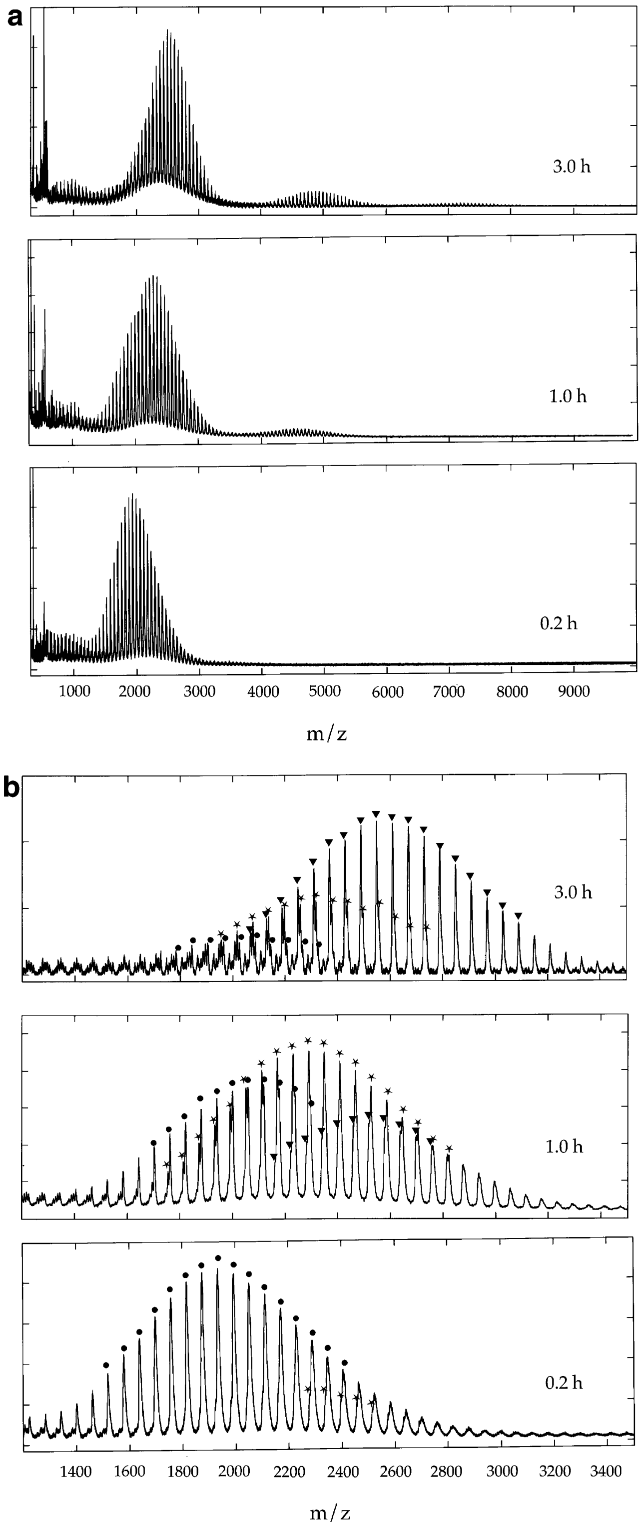


Figure 2. MALDI TOF spectra of MeOH end-capped PPG prepolymers prepared at 108 °C for different amounts of time: (a) entire mass range; (b) mass range in the region of the major products. Circles are from monomers, stars are from dimers, and triangles are from trimers.

To determine the number and weight molecular weight distributions in this model adhesive system, a combination of MALDI−TOF mass spectrometry and SEC was used. The results are shown in Figures 2 and 3 for MeOH end-capped prepolymers prepared at 108 °C. The experimental data are then compared to what is expected theoretically. In the absence of side reactions, the number fraction (N_i) and weight fraction (W_i) of each oligomer can be determined as first described by Flory.[26] Equations describing the population (number fraction or weight fraction) of each oligomer formed during the step polymerization of PPG with excess MDI are the following:

For HO−(PPG-MDI)$_n$−NCO

$$N_x = p^{x-1} r^{x/2} \left[\frac{2(1-p)(1-rp)}{\left(1 + \frac{1}{r} - 2p\right) r} \right] \tag{1}$$

$$W_x = x p^{x-1} r^{x/2} \left[\frac{2(1-p)(1-rp)}{1+r} \right] \tag{2}$$

For HO−(PPG-MDI)$_n$−PPG−OH

$$N_y = p^{y-1} r^{y/2} \left[\frac{(1-p)^2 r^{-1/2}}{1 + \frac{1}{r} - 2p} \right] \tag{3}$$

$$W_y = y p^{y-1} r^{y/2} \left[\frac{(1-p)^2 r^{-1/2}}{1+r} \right] \tag{4}$$

For OCN−MDI−(PPG-MDI)$_n$−NCO

$$N_z = p^{z-1} r^{z/2} \left[\frac{(1-rp)^2 r^{-3/2}}{1 + \frac{1}{r} - 2p} \right] \tag{5}$$

$$W_z = z p^{z-1} r^{z/2} \left[\frac{(1-rp)^2 r^{-1/2}}{1+r} \right] \tag{6}$$

At incomplete conversion, a mixture of OH and NCO end-capped oligomers will have been formed, while at complete conversion, only NCO end-capped species will exist. Separate relationships are necessary to describe the relative abundance of these species, where even oligomers are those species terminated with both NCO and an OH and odd oligomers can be terminated with either two NCO's or two OH's.

With increasing conversion, obvious changes in the MALDI−TOF spectra are observed corresponding to the formation of different oligomers (Figure 2a). At a low degree of conversion, the sample obtained after a reaction time of 0.2 h, the majority of the prepolymer still has a molecular weight that centers around 2000 g mol^{-1}. As conversion increases, several higher molecular weight distributions are observed. After 3 h (ρ_{OH} = 0.97), four main distributions are evident with M_P of 2548, 4867, 7180, and 9320 g mol^{-1}. These distributions correspond to trimer (i.e., MDI−PPG−MDI), pentamer, heptamer, and nonomer. Under the experimental conditions used, three additional distributions are observed in the mass range from 1200 to 3400, as shown in Figure 2b, which correspond to the Na+ adducts of monomer (PPG), dimer (PPG−MDI), and trimer (MDI−PPG−MDI). Below 800 *m*/*z*, peaks can be observed corresponding to MeOH end-capped MDI monomer and uretidinedione dimer and the matrix.

Owing to the narrow polydispersity of PPG, oligomer species with different numbers of PPG units are resolvable in SEC (Figure 3a). Unlike in MALDI−TOF, however, increasing the number of MDI units in an oligomer does not give a discrete change but rather a shift in the peak elution volume (i.e., molecular weight). Thus, in the trace at 1.0 h, the discrete peaks at 19.52, 18.50, and 18.12 mL correspond to species with 1, 2, and 3 PPG units, respectively. The shift in peak elution volume for the 0.2 h reaction vs the 1.0 h reaction from 19.76 to 19.52 mL corresponds to a change in the relative distribution of monomer, dimer, and trimer in each sample. The weight fraction distributions (Figure 3b) were calculated from the calibration curve shown in Figure 1. As expected, the weight fraction of MDI monomer and low PPG oligomers decreases with conversion as higher oligomers are formed. Additionally, the small peak corresponding to the MDI dimer is observed to decrease with conversion, suggesting that these molecules are also incorporated into the prepolymer chains.

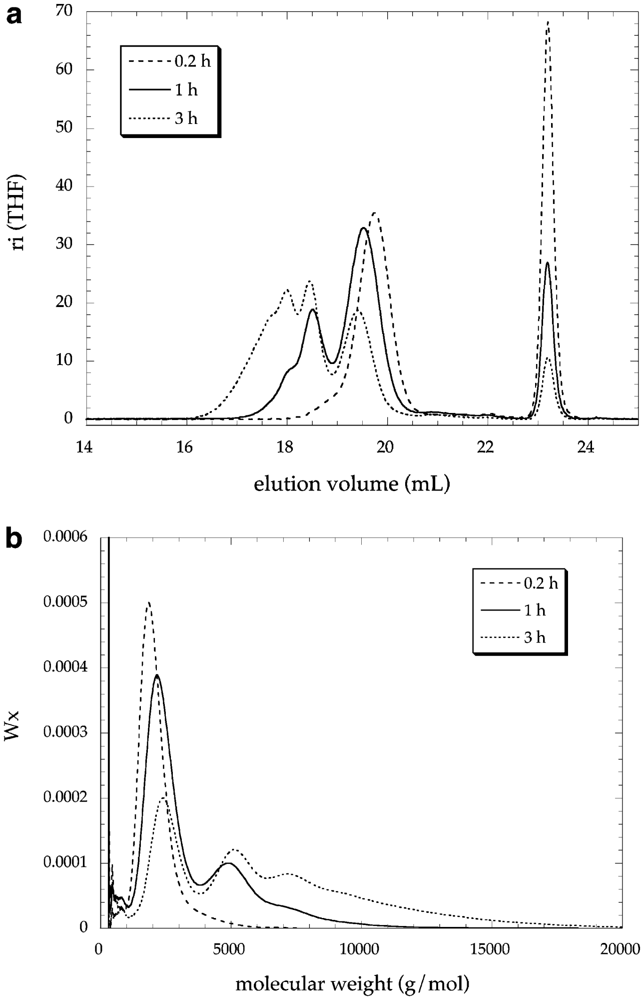


Figure 3. Results from SEC of MeOH end-capped PPG prepolymers prepared at 108 °C for different amounts of time: (a) SEC traces; (b) weight fraction distributions.

To compare MALDI−TOF and SEC data with step polymerization theory, the number fraction and weight fraction distributions must first be determined. The MALDI−TOF results can be separated into several different distributions, depending on the number of PPG units in the oligomer. The number fractions determined by integration of these distributions can be compared with those determined by eqs 1−6. Neglecting the contribution from the free MDI (see above) in our calculations, the results are shown in Figure 4a. Although the overall trend of increasing molecular weight as a function of conversion is predicted, a quantitative agreement is absent. The data reflect an over-representation of low molecular weight oligomers. The theory assumes that all molecules are difunctional, that reactivity is independent of molecular size, and that only

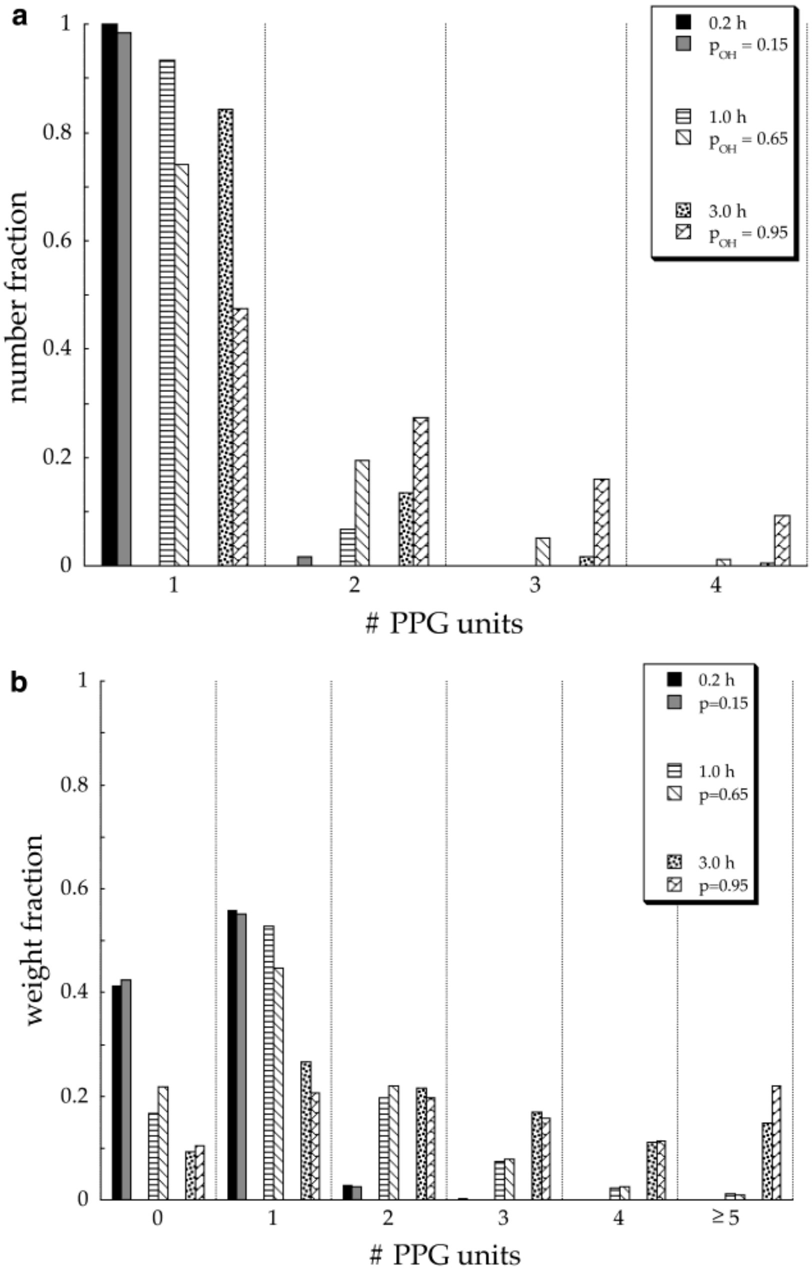


Figure 4. Molecular weight distribution determined from MALDI TOF and SEC data and compared with results from Flory's step polymerization theory: (a) number fraction distribution; (b) weight fraction distribution.

linear polymerization occurs. These assumptions are not likely to cause the significant differences observed. Instead, it is most likely due to inherent experimental errors. It has been shown that small perturbations in end groups can have a large effect on ionization efficiency.[27] In addition, instrumental effects can lead to a mass bias during the MALDI desorption/ionization process.[28]

The SEC weight fraction data were in surprisingly good agreement with the predictions. As described above, the data were divided into several distributions, depending on the number of PPG units in the oligomer: 0 (MDI monomer and dimer), 1, 2, 3, 4, and ≥5. The amount in each group was determined by integrating the plots in 2200 g/mol intervals. This method yielded more consistent results than those involving more sophisticated but laborious deconvolution routines. The results are shown in Figure 4b. The agreement is quite good with the differences in most cases being approximately 10%. For the two prepolymers at higher conversions, the same trend is observed. More low molecular weight oligomers are observed than predicted. The PPG monomer contained approximately 5% monofunctional materials. Upon reacting with MDI, these chains would maintain a molecular weight similar to dimers. This may be one source of inconsistency. The weight fraction of 0 PPG materials is always lower than predicted. This may be due to the choice of detector, a differential refractometer using THF as an eluant ($n = 1.407$). The refractive indices of PPG and MDI are 1.447 and 1.580, respectively. The difference apparently has only a minimal effect as the weight fraction MDI in each higher oligomer changes but is more substantial for materials containing only MDI. The results obtained from SEC suggest that the molecular weight distribution agree with the step polymerization theory. One could predict a priori the amount of free MDI needed for hard segment formation.

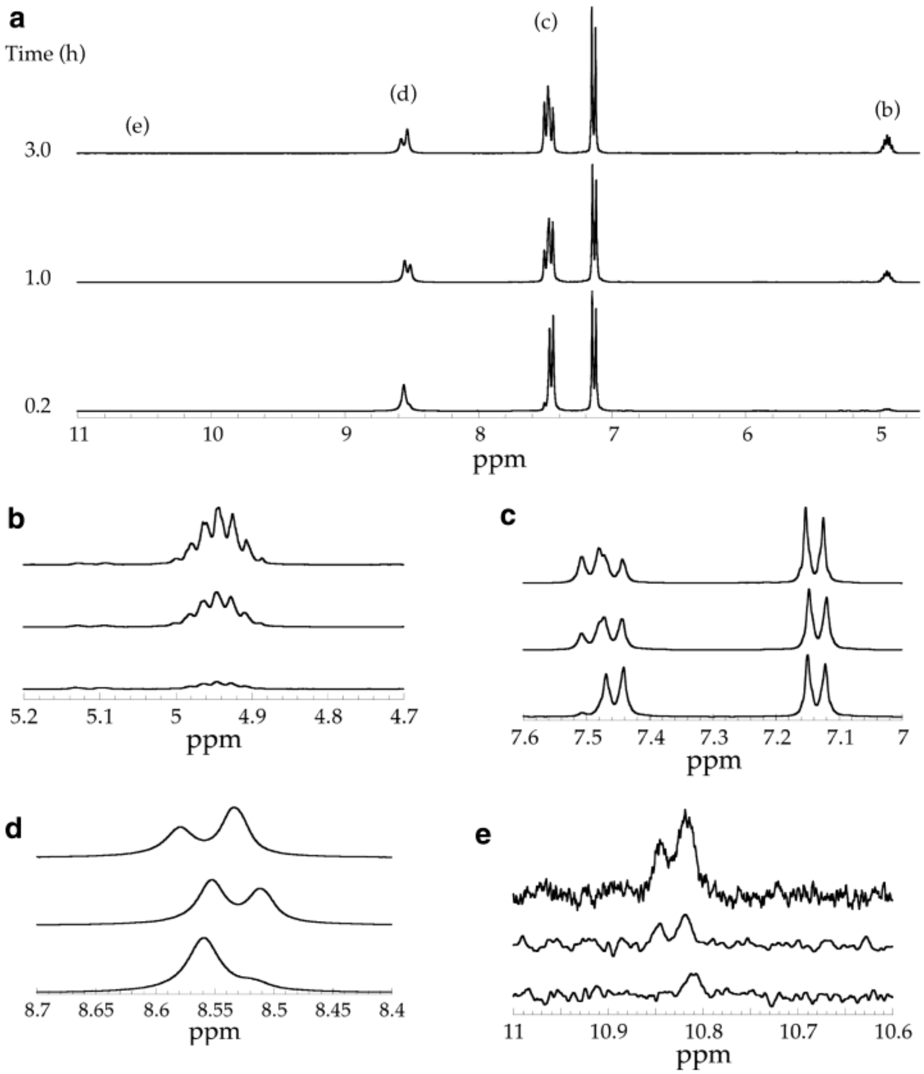


Figure 5. ^{1}H NMR spectra of MeOH end-capped PPG prepolymers prepared at 108 °C for different amounts of time: (a) portion of spectrum used for analysis, normalized to aromatic protons; (b) PPG methyne α to carbamate; (c) aromatic H; (d) urethane NH; (e) allophanate NH.

As mentioned above, the presence of side reactions may alter the structure considerably. ^{1}H NMR is perhaps the most suitable technique for quantification of the amount of side products. Urethane, allophanate, urea, and biuret NH's all have unique resonances.[29] Their positions depend largely on the nature of the degree of hydrogen bonding, which is influenced by solvent choice, water content, and concentration.[30] For quantitative analysis of NH resonances, exchangeable solvents such as $CDCl_3$ or D_2O obviously should not be used.

To determine the percentage of N (i.e., NCO groups) that participates in side reactions, the ^{1}H NMR spectra were collected in acetone-d_6. The data obtained for methanol end-capped prepolymers are shown in Figure 5a. The main region used for analysis is that from 4.5 to 11.0 ppm, which focuses on the MDI unit. The ratio of OH/NCO remains fixed in each reaction, and since each side reaction maintains the phenyl ring intact, the total number of phenyl ring protons will remain constant. This region is then used as an internal standard to carry out a quantitative analysis.

With increasing conversion, several changes are evident. Figure 5b shows a complex resonance at 4.95 ppm, which can be assigned to the PPG chain's end methyne proton after reaction. Its intensity increases with conversion, as more of these units are formed. The region from 7 to 7.6 ppm corresponds to those resonances arising entirely from aromatic protons as shown in Figure 5c. Close examination shows that this region is also sensitive to conversion. The region arising from carbamate NH is shown in Figure 5d.[29] The narrow lines observed in acetone-d_6 allow resolution of the two different carbamate species: those arising from reacted NCO and those arising from unreacted NCO that have been end-capped with methanol. On the basis of the changes in the spectra observed with increasing conversion, the higher field resonance can be attributed to the PPG carbamate. There has been controversy regarding the validity of using NH resonances for quantitative analysis, so the intensity observed in this region was confirmed by using it to calculate the conversion.[31] After deconvolution, ρ_{NCO} can be determined, as shown in Table 1. Within the experimental error, the degree of conversion is consistent with the titration value.

The integrals of the various resonances are shown in Table 3. In the absence of side reactions, every urethane proton is associated with four phenyl ring protons. Additional isocyanate or urethane consuming reactions will alter this ratio. As can be seen from Table 3, the

Table 2. Results from the Analysis of ^{1}H NMR Spectra for Prepolymers Prepared at 108 °C

	integrals from ^{1}H NMR in acetone-d_6		
time (h)	aromatics	urethane × 4	allophanate × 8
0.2	1.00	0.888	0.000
1.0	1.00	0.901	0.003
3.0	1.00	0.888	0.009

Table 3. Results for PPG Prepolymers Prepared under Different Reaction Conditions

temp (°C)	time (h)	ρ_{NCO} (titration)	ρ_{OH} (titration)	ρ_{OH} (NMR in pyr)	allophanate (% N)
108	1.0	0.3984	0.6471	0.60	0.6
108	3.0	0.6000	0.9677	0.95	1.8
122	1.0	0.50	0.81	0.79	1.4
122	3.0	0.662	1.052	>0.95	3.5
145	1.0	0.5935	0.9707	0.93	5.6
145	3.0	0.6602	1.0788	>0.95	10.2

fraction of MDI nitrogen characterized by urethane is between 89 and 90%. The remaining 10% must be involved in other types of linkages, as shown in Scheme 2. Several of these linkages contain nitrogen-bound protons, for example allophanate, urea, and biuret. On the other hand, uretedinedione and isocyanurates do not contain NH. Thus, while these linkages will contribute intensity to the aromatic region, they will not display any other characteristic resonances in ^{1}H NMR.

The resonances that can be assigned to allophanate NH are shown in Figure 5e.[29] At this reaction temperature, the number of these linkages is relatively small. It is evident that with increasing time the intensity at 10.2 and 10.85 ppm increases. The amount of allophanate is determined by first accounting for the eight aromatic protons associated with this linkage. Then the total percentage of N that formed allophanates will be twice this number, since two N are involved in that linkage. At 108 °C for a reaction time of 3.0 h (98% conversion), only 1.8% of N has formed allophanate. This is consistent with the amount of allophanate determined by a titration method for PPG prepolymers prepared in the melt.[32]

The MDI used in this study contained 2% uretidinedione. The sum of this species plus the urethane, allophanate, and urea populations should equal 1.0. In fact, the amount we observe is always closer to 0.93. This would suggest that other linkages are forming during synthesis. However, combined with the titration data, it seems unlikely that the remaining 7% arises from other side products. Model studies have shown that, in the absence of catalyst, the population of isocyanurate is much less than the population of allophanate.[16] We also examined the rate of dimerization of MDI at 108 °C and found that after 8 h only 2% of the N had been converted to uretidinedione. At present, it is not possible to account for the “missing” 7%. Nonetheless, the amount of the principal side product, allophanate, can be quantified using NMR analysis.

Effect of Reaction Temperature. A combination of ^{1}H NMR and SEC as described above is used to examine the formation of PPG-based prepolymer as a function of reaction time and temperature. Three reaction temperatures (108, 122, and 145 °C) were chosen since they correspond to the range generally used in most applications. Reactions were carried out for 1−3 h (Table 3). One hour is insufficiently long to allow complete reaction, except for the sample at 145 °C. A reaction time of 3 h allows complete conversion or nearly complete conversion.

As discussed above, titration detects the number of NCO groups. Calculation of ρ_{OH} is indirect and assumes no side reactions. The values obtained for 122 and 145 °C are greater than 1.0, thus yielding clear evidence that other NCO-consuming side reactions must be taking place. An additional 5.2% and 7.9% of NCO's are being consumed by side reactions.

Using ^{1}H NMR spectroscopy, the percentage of N forming allophanate linkages can be determined (Table 3). Clearly, both reaction time and temperature have a dramatic effect on the allophanate population. For the sample reacted at 108 °C, the amount of allophanate is nearly negligible with only 1.8% of N forming allophanates. Even after 3 h at 122 °C, the amount of allophanate formed remains fairly low. The amount observed is 1.4 and 3.5% for reaction times of 1 and 3 h, respectively. At 145 °C, however, this reaction is no longer a negligible one. Comparing two prepolymers at similar conversion (122 °C, 3 h vs 145 C, 1 h), the one prepared for a shorter reaction time at 145 °C contains a higher allophanate content. After 3 h, the amount reaches 10%. In this case, the viscosity is noticeably higher. Other adhesive properties may be influenced as well.

Additionally, other side reactions must be taking place. As stated above, the error in the titration and the ^{1}H NMR is about 0.2 and 5.0%, respectively. Given that each allophanate linkage consumes 1 equiv of urethane (already accounted for in the titration) and 1 equiv of isocyanate, the number of additional reactions can be deduced from the titration data. Approximately 3% of the NCO groups are consumed by another reaction.

SEC results can be combined with the data from NMR to determine how side reactions perturb the molecular weight distribution. Since the effects of conversion have already been discussed in the preceding section, this part will focus on the three samples that have reached similar conversions, i.e., those prepared at 96, 122, and 145 °C for 3 h. The results are shown in Figure 6. Several conclusions can be reached. The prepolymers prepared at higher reaction temperatures, and thus having larger allophanate content, exhibit higher overall molecular weight. Second, M_P of the main oligomer distribution near 2500 g mol^{-1} shifts to slightly higher molecular weight (from 2300 to 2400), suggesting that the incorporation of allophanate linkages into trimer molecules is occurring. Finally, the discrete distributions that were evident at 108 °C are converted to broader distributions as allophanates are formed between chains of various molecular weights.

Because of the breadth of these distributions, the change in weight fraction was calculated for different ranges: 0 PPG, 1 PPG, 2 PPG, and ≥3 PPG. The results are shown in Figure 7a,b. As the temperature is increased, the amount of 1 and 2 PPG-containing oligomers progressively decreases. On the other hand, the amount of free MDI decreases and appears to reach a constant value. High molecular weight species progressively increase. The conclusion based upon these observations is that free MDI is not preferentially consumed to form allophanates. Under these reaction conditions, it appears that it is equally favorable for both low and high molecular weight species to participate in the reaction.

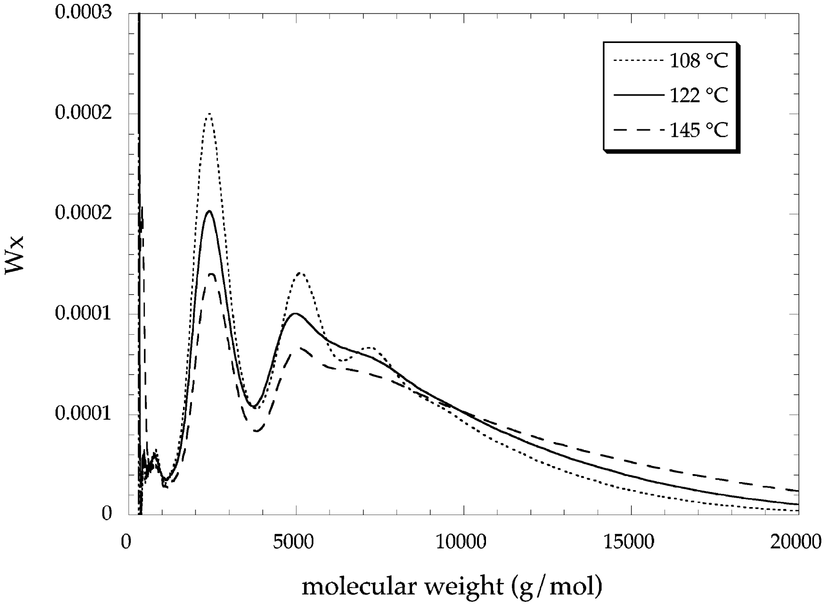


Figure 6. Weight fraction distributions obtained from SEC data of MeOH end-capped PPG prepolymers prepared at different temperatures.

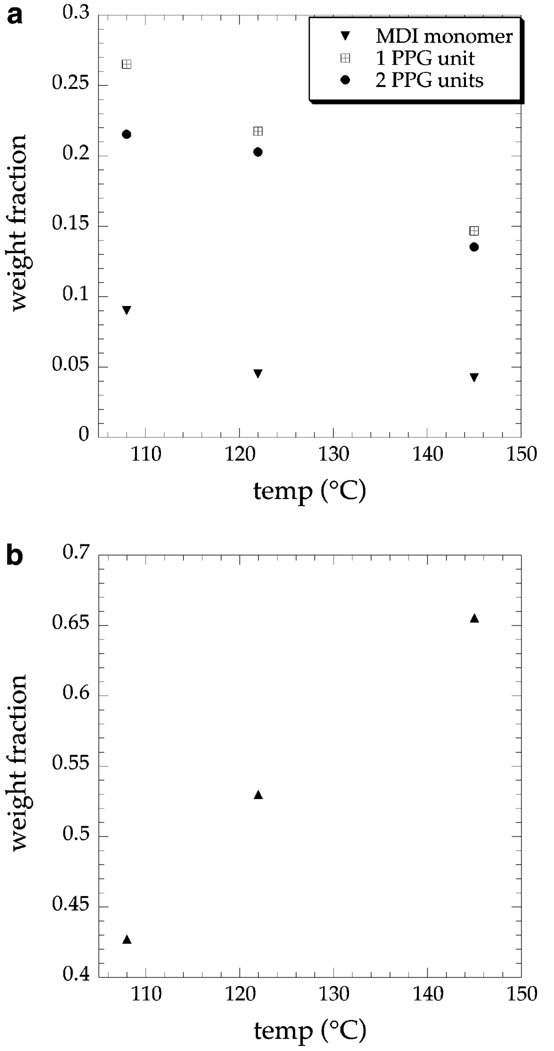


Figure 7. Change in oligomer weight fraction with increasing temperature (increasing amounts of allophanate): (a) low molecular weight species from 300 to 6000 g mol^{-1}; (b) high molecular weight species from 6000 to 35 000 g mol^{-1}.

Conclusions

The polyurethane system that we have focused on in this study, i.e., the formation of prepolymers in adhesives, involving the reaction of poly(propylene glycol) with isocyanate, has yielded a number of intriguing data. The two aspects given particular emphasis are the molecular weight distribution and the amount and type of side reactions. Using a combination of three characterization techniques (NMR, SEC, and mass spectrometry), the polymerization process at various temperatures (108−145 °C) has been determined. The extent of reaction was highly dependent on reaction temperature. The molecular weight distributions achieved at each temperature have been measured and are consistent with the ones based upon a step polymerization mechanism. Changes in distribution as a function of extent of reaction have also been established. The side products present can be derived from mass balance analysis and, in more detail, using NMR analysis. The formation of allophanates is highly dependent on reaction temperature. With modest increase in reaction temperature, the amount of allophanates can increase from negligible to over 10% of all nitrogen-containing compounds. This study demonstrates that the products formed can be studied in a quantitative fashion. The commercial systems usually employ other polymers, such as various crystallizable polyesters, and compatibilizers, such as acrylate copolymers. The structure of those polymers is also of high interest and will be reported in the future.

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